

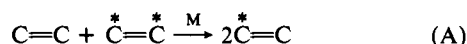
# Olefin Metathesis. A Mechanistic Study of High-Valent Group 6 Catalysts

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**Abstract:** The results of an ab initio theoretical mechanistic study are used to suggest that oxo-alkylidene complexes are the active, chain-carrying metathesis catalysts for high-valent Mo, W, and Re complexes and that the oxygen ligand is intimately involved in the catalytic process. Furthermore, we suggest that oxo-alkylidene complexes are formed on supported molybdate and tungstenate catalysts and that dioxo precursors can provide a convenient route to formation of well-defined surface catalysts for olefin metathesis and oxidation reactions. The spectator oxo group is suggested to play a central role in stabilizing the critical intermediate in these reactions and may be important in other reactions of metal oxides (e.g.,  $\text{MnO}_4^-$ ,  $\text{OsO}_4$ ,  $\text{RuO}_4$ , supported transition-metal oxides).

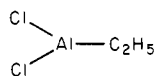
One of the most intriguing and best studied catalytic reactions in organometallic chemistry is the olefin metathesis reaction.<sup>1</sup> It is of potential synthetic utility<sup>2</sup> and is of industrial importance.<sup>3</sup> Formally, the reaction involves a simultaneous cleavage of two olefin double bonds followed by the formation of the alternate double bonds



where M is an appropriate metal complex. The currently accepted mechanism involves a metal-alkylidene (carbene) complex (that is,  $\text{M}=\text{CR}_2$ ) as the active chain-carrying catalyst that reacts with an olefin to form a metallacyclobutane intermediate (a of Scheme I) that decomposes to form the product olefin (b of Scheme I). This mechanism was proposed by Herrison and Chauvin<sup>4</sup> and has been established through detailed (and ingenious) study of isotopic scrambling (Grubbs<sup>5</sup> and Katz<sup>6</sup>) and by indirect evidence such as the synthesis of metallocarbenes (Schrock<sup>7</sup>) and metallacyclobutanes (Green,<sup>8</sup> Puddephatt,<sup>9</sup> Whitesides,<sup>10</sup> and Ibers<sup>11</sup>) and by the analysis of the character of polymeric products of cycloolefins (Casey<sup>12</sup>). Furthermore, Casey<sup>13</sup> has synthesized low-valent metallocarbenoid complexes [ $\text{W}(\text{CO})_5\text{CPh}_2$ ] that stoichiometrically metathesize olefins. Potential chain-terminating side reactions are the unimolecular decomposition of the metallacycle (reductive elimination), forming a cyclopropane plus the reduced metal complex (c of Scheme I), and the bimolecular decomposition of the carbene complex (d of Scheme I).

As indicated above, that are two general classes of complexes used to mechanistically investigate olefin metathesis: (1) high-valent (generally  $d^0$ ) complexes of Mo, W, and Re (these are generally catalytic and often industrially important) and (2) low-valent complexes of Cr, Mo, and W (oxidation state zero) (these have been significant in determining the general mechanism for the metathesis reaction but are generally not catalytic and have been of little industrial importance). There are significant differences between the high- and low-valent systems, particularly in the nature of the metal-CR<sub>2</sub> bond. Since only the high-valent class of metathesis complexes have been established to be truly catalytic, this paper will deal exclusively with this type.

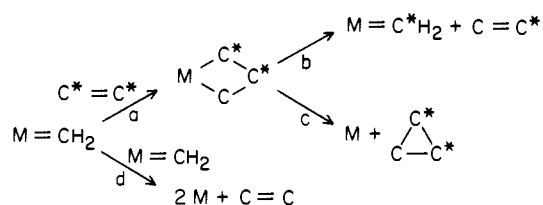
Typical recipes for active homogeneous<sup>14</sup> high-valent Mo, W, and Re metathesis catalysts involve a combination of various sources of metal [M(0) through M(VI)] with Lewis acids such as



under a variety of conditions. A result of this diversity is that a detailed understanding of the ligand environment and even the

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Scheme I



oxidation state of the active catalyst (if there is just one active catalyst) is still lacking. Since the true catalyst is probably in small concentration,<sup>15</sup> direct experimental studies on the catalytic system are quite difficult. Further, the industrially important catalysts consist of a metal oxide on an inorganic support, providing additional difficulties for physical studies. In fact, for supported catalysts it has been shown by Hall<sup>16</sup> that the metathesis sites

- (1) (a) R. H. Grubbs, *Prog. Inorg. Chem.*, **24**, 1-50 (1978); (b) N. Calderon, J. P. Lawrence, and E. A. Ofstead, *Adv. Organomet. Chem.*, **17**, 449-492 (1979).
- (2) J. Tsuji and S. Hashiguchi, *Tetrahedron Lett.*, **21**, 2955-2958 (1980).
- (3) G. W. Parshall, "Homogeneous Catalysis"; Wiley, New York, 1980, pp 174-176.
- (4) J. L. Herisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161-176 (1970).
- (5) R. H. Grubbs, P. L. Burk, and D. D. Carr, *J. Am. Chem. Soc.*, **97**, 3265-3267 (1975); R. H. Grubbs, D. D. Carr, C. Hopplin, and P. L. Burke, *ibid.*, **98**, 3478-3483 (1976).
- (6) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **97**, 1592-1594 (1975); T. J. Katz, J. McGinnis, and C. Altus, *ibid.*, **98**, 606-608 (1976).
- (7) R. R. Schrock, *J. Am. Chem. Soc.*, **96**, 6796-6797 (1974); *ibid.*, **98**, 5399-5400 (1976); R. R. Schrock and P. R. Sharp, *ibid.*, **100**, 2389-2399 (1978).
- (8) M. Ephritikhine, M. L. H. Greene, and R. E. MacKenzie, *J. Chem. Soc., Chem. Commun.*, 619-621 (1976); M. Ephritikhine, B. R. Francis, M. L. H. Green, R. E. MacKenzie, and M. J. Smith, *J. Chem. Soc., Dalton Trans.*, 1131-1135 (1977).
- (9) R. J. Puddephatt, M. A. Quyser, and C. F. H. Tippar, *J. Chem. Soc., Chem. Commun.*, 626-627 (1976).
- (10) P. Foley and G. M. Whitesides, *J. Am. Chem. Soc.*, **101**, 2732-2733 (1979).
- (11) J. Rajaram and J. A. Ibers, *J. Am. Chem. Soc.*, **100**, 829-838 (1978).
- (12) C. P. Casey and R. L. Anderson, *J. Chem. Soc., Chem. Commun.*, 895 (1975).
- (13) (a) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833-5834 (1973); (b) *ibid.*, **96**, 7808-7809 (1974); (c) C. P. Casey, L. D. Albin, and T. J. Burkhardt, *ibid.*, **99**, 2533-2539 (1979).
- (14) (a) It has been suggested that the catalysts thought to be homogeneous may actually be heterogeneous; see, for example, ref 1a; (b) Y. Uchida, M. Hida, and T. Tatsumi, *Bull. Chem. Soc. Jpn.*, **45**, 1158 (1972).
- (15) Indications are that the active catalyst has a rapid bimolecular decomposition pathway, and hence a stable catalytic system must have the catalyst in small concentration. See, for example, ref 7.
- (16) E. A. Lombardo, M. LoJacono, and W. K. Hall, *J. Catal.*, **64**, 150-162 (1980).

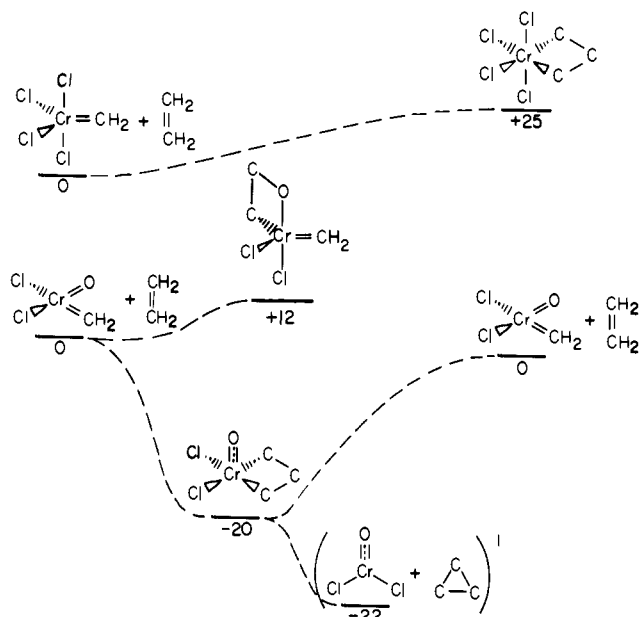


Figure 1. Energetics ( $\Delta G_{300}$  in kcal/mol) for the reaction of  $C_2H_4$  with the carbene and oxo-alkylidene of Cr.

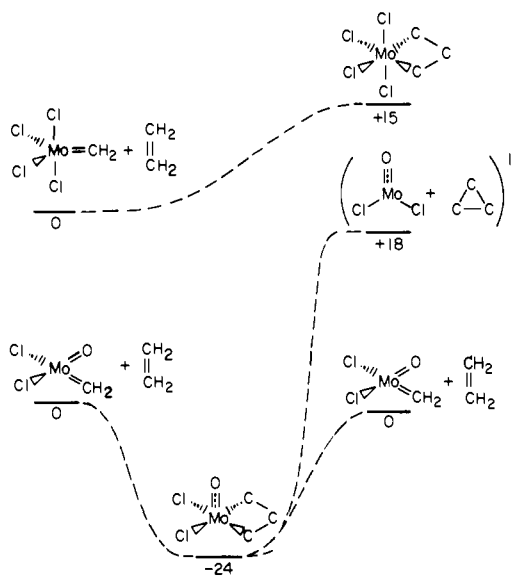
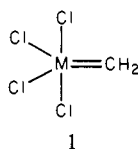


Figure 2. Energetics ( $\Delta G_{300}$  in kcal/mol) for the reaction of  $C_2H_4$  with the carbene and oxo-alkylidene of Mo.

correspond to less than 1% of the Mo present at the surface. The theoretical calculations presented here<sup>17</sup> will concentrate on determining the detailed ligand environment of high-valent metathesis catalysts, developing an understanding of why particular ligands are desirable, and suggesting a mechanistic understanding of the initiation step for supported catalysts.

### Theoretical Studies

Since  $WCl_6$  can be used as the starting point for metathesis catalysts,<sup>18,19</sup> the simplest catalyst consistent with Scheme Ia is



(17) A preliminary account of this work has been published; see A. K. Rappé and W. A. Goddard, III, *Nature (London)*, **285**, 311–312 (1980); *J. Am. Chem. Soc.*, **102**, 5114–5115 (1980). For additional details, see A. K. Rappé, Ph.D. Thesis, California Institute of Technology, Oct 1980.

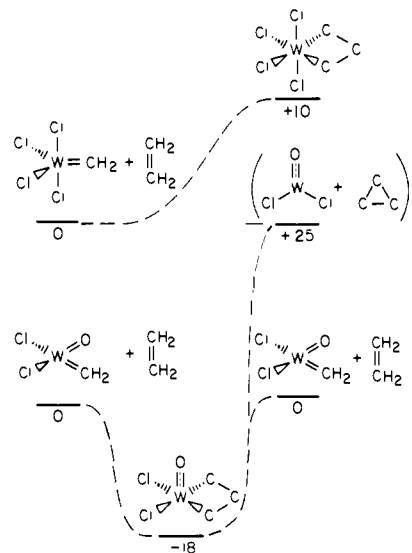
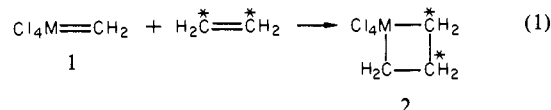


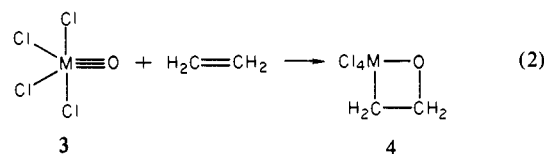
Figure 3. Energetics ( $\Delta G_{300}$  in kcal/mol) for the reaction of  $C_2H_4$  with the carbene and oxo-alkylidene of W.

Thus, as the first step in our studies, we examined the cycloaddition step postulated in the Herrison–Chauvin mechanism (1). As



indicated in Figures 1a, 2a, and 3a, we find that process 1 is *not* favorable, with  $\Delta G_{300} = +25$ ,  $+15$ , and  $+10$  kcal mol<sup>-1</sup> for  $M = Cr$ ,  $Mo$ , and  $W$ , respectively.<sup>20–22</sup> The bonding in the metallacycle is not strong enough to compensate for the loss of the  $\pi$  bonding.

**A. Bonding in Mono- and Dioxo Systems.** In order to learn more about such metallacycle formations and possible initiation steps for supported catalysts, we considered<sup>17</sup> some related processes, (2) and (3). Here we found that reaction 2 is quite



(18) J. M. Basset, G. Coudurier, R. Mutin, H. Proliaud, and Y. Trambouze, *J. Catal.*, **34**, 196–202 (1974).

(19) M. T. Mocella, R. Rovner, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1689–1690 (1976).

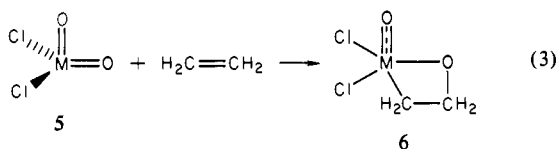
(20) The calculations<sup>21</sup> were all-electron ab initio by using a valence double- $\zeta$  basis on all centers except for the Cl. The Cl was described by using the SHC effective core potential<sup>22</sup> to replace the Ne core and a valence basis that was contracted to minimum basis for  $TiCl_4$ . Generalized valence bond (GVB) calculations were carried out, correlating all bonds to the metal except for metal–Cl bonds. These GVB orbitals were then used in a full configuration interaction (GVB–CI) calculation for each molecule, leading to the energies used to obtain  $\Delta E$  for the various processes.<sup>23</sup> Vibrational frequencies (estimated, experimental, or calculated) were used with  $\Delta E$  to obtain  $\Delta H$  at 0 K and were also used in conjunction with moments of inertia to calculate  $C_p$  and thereby  $\Delta H$  at 300 K and also to generate  $\Delta S$ , which were used to obtain the  $\Delta G_{300}$ .

(21) A detailed analysis of basis set and correlation effects is provided in A. K. Rappé and W. A. Goddard III in "Potential Energy Surfaces and Dynamics Calculations", D. G. Truhlar, Ed., Plenum Press, New York, 1981, pp 661–684.

(22) A. K. Rappé, T. A. Smedley, and W. A. Goddard, III, *J. Phys. Chem.*, **85**, 1662 (1981).

(23) These calculations do not use  $f$  functions. Related calculations<sup>21</sup> on  $Cl_2Ti=O$  and  $Cl_2TiH_2$  indicate that omission of these functions weakens the  $M=O$  bond by 5.2 kcal and the two  $M-H$  bonds by a total of 5.1 kcal. For  $Cl_4Mo=O$ , the experimental value of the  $Mo-O$  bond is 106.5,<sup>24</sup> about 4.5 kcal higher than the value obtained without  $f$  functions.

(24) N. Sano and G. R. Belton, *Metal. Trans.*, **5**, 2151 (1974).



endothemic,  $\Delta G_{300} = +54$  and  $+49$  kcal mol<sup>-1</sup> for Cr and Mo, respectively, whereas reaction 3 is quite exothermic,  $\Delta G_{300} = -14$  and  $-21$  kcal mol<sup>-1</sup> for Cr and Mo, respectively. Further analysis of the wave functions shows that these differences arise from a fundamental difference in the metal-oxo bonds for the monooxo species 3 as compared to the dioxo species 5.

In the dioxo species each oxo group makes a  $\sigma$  bond and a  $\pi$  bond to the metal, leaving a nonbonding lone pair on the oxygen perpendicular to the bond axis (a normal nonbonding oxygen lone pair just as in a ketone). The orbitals for one of the metal-oxo bonds are shown in Figure 4. Thus, of the six valence electrons on the metal, two are involved in partially ionic  $\sigma$  bonds to the two Cl, two are involved in covalent  $\sigma$  bonds to the two oxygens, and two are involved in covalent  $\pi$  bonds to the two oxygens.

In the monooxo species, four of the six valence electrons on the metal are involved in partially ionic  $\sigma$  bonds to the four Cl and two are involved in bonds to the oxygen. However, in this case the stable configuration has both of these latter electrons in  $d\pi$  orbitals making two covalent  $\pi$  bonds with the oxygens (see Figure 5bc), while the lone pair on the oxygen is aligned with the bond axis ( $\sigma$ ) pointing at the empty  $d\sigma$  orbital of the metal (see Figure 5a). The result is a triple bond involving two electrons from the metal and four from the oxygen, quite analogous to the bond in CO. The dioxo system cannot make this triple bond since use of both  $\pi$  orbitals for a triple bond to one oxo group would deprive the second oxygen of the  $\pi$  orbitals for its bonds (further, the  $\pi$  orbital needed to make a second  $\pi$  bond to one oxo group is destabilized by the lone-pair orbital on the second oxo group and by the metal-O  $\sigma$  bond). This situation for the dioxo complex is analogous to CO<sub>2</sub> where there is only a double bond to each oxygen, whereas the monooxo complex makes a triple bond just as in CO.

The energetic consequence of these effects is that the M=O bond of the monooxo species 3 is 82 kcal for Cr and 102 kcal for Mo, whereas the M=O bond in the dioxo species is 51 kcal for Cr and 79 kcal for Mo. Thus the triple bond is 31 kcal stronger than the double bond for Cr and 23 kcal stronger for Mo.

The larger strength (31 kcal for Cr, 23 kcal for Mo) in the metal-oxo bond of 3 vs. that of 5 explains part of the difference between reaction 2 and reaction 3 (total difference 68 kcal for Cr and 60 kcal for Mo); however, this accounts for only about half the difference and indeed, including only this effect, reaction 3 would still be quite endothermic. The critical effect responsible for making 3 exothermic has to do with a change in character of the second oxo group (the spectator oxo group) in 5 upon forming the metallacycle with the other oxo group. In order to understand the origin of this effect, compare the metallocycle species 6 with the monooxo species 3. Both have four  $\sigma$  bonds plus one metal-oxo bond, and consequently both systems can use both  $\pi$  orbitals on the metal to make a triple metal-oxo bond. Thus, in reaction 3 the *spectator oxo group* of 5 (the oxygen is *not* involved in the reaction) changes from a double bond in 5 to a triple bond in 6, stabilizing the metallacyclic intermediate 6. It is this *spectator oxo stabilization* that makes the metallacycle formation favorable for (3).

It should be emphasized that for the double-bond-to-triple-bond conversion to occur it is essential for the metal to form two auxiliary, partially ionic bonds to electronegative ligands (such as halides or alkoxides) so that the metal-oxo bonds are covalent. In the absence of such ligands, the metal-oxo  $\sigma$  bonds will be partially ionic, effectively preventing the conversion to a triple bond. (This occurs because O<sup>-</sup> has only one singly occupied orbital to form a covalent  $\pi$  bond.) In addition, the configuration of the metal must allow an empty  $d\sigma$  orbital in order to form the donor-acceptor  $\pi$  bond. Consequently, this effect is favored only

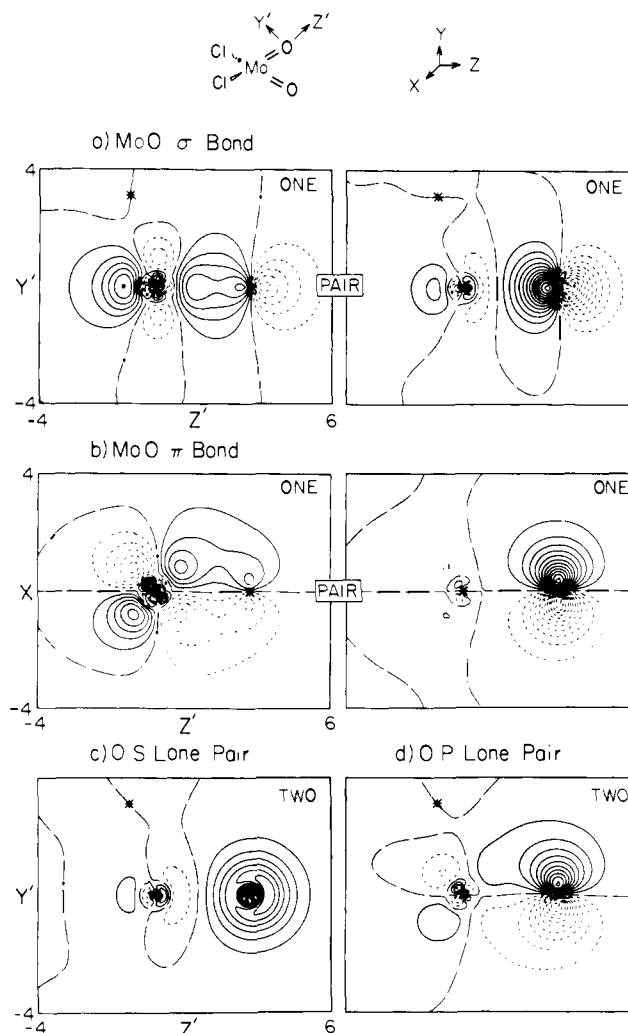
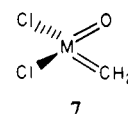


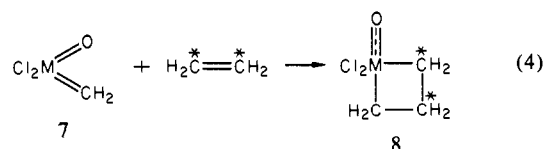
Figure 4. The GVB orbitals involved in the bond to one oxo group of  $(\text{Cl})_2\text{Mo}(\text{=O})_2$ . The long dashes indicate zero amplitude and dotted lines indicate negative amplitude. The spacing between contours is 0.0625 au.

for the left portion of the transition elements.

**B. The Oxo-Alkylidene and Metallacycle Formation.** The above studies suggested to us<sup>17</sup> that an oxo-alkylidene

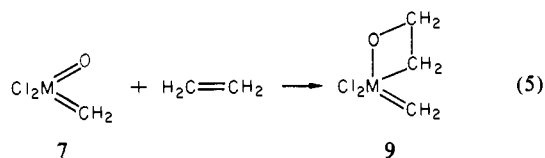


would favor formation of metallacycles



because of conversion of the double-bond spectator oxo group in 7 to a triple bond in 8. Indeed, as shown in Figures 1b, 2b, and 3b, the calculations<sup>17</sup> lead to just this result, with  $\Delta G_{300} = -20$ ,  $-24$ , and  $-18$  kcal for M = Cr, Mo, and W, respectively. On the other hand, the potential side reaction is much less favorable ( $\Delta G = +12$ ,  $+2$ ,  $+0$  kcal for M = Cr, Mo, and W, respectively) because here the spectator group is an alkylidene that provides only a double bond in both 7 and 9.

As a result of these studies, we have suggested<sup>17</sup> that the oxo-alkylidene 7 is the active intermediate in the high-valent



metathesis catalysis by Mo and W. Further, the active metathesis catalyst for the Re system<sup>14b</sup> is suggested to be a trichloro-oxo-alkylidene complex.

**C. Comments on Electronic Structure.** In normal oxidation state formalism, the metal in **3** or **5** would be considered to be fully oxidized, M(VI), the oxo groups would be considered as O<sup>2-</sup>, and the chlorides as Cl<sup>-</sup>. Thus the metal is described as d<sup>0</sup>. Similarly, the alkylidene in **1** or **7** would be considered as <sup>2-</sup>CR<sub>2</sub> and the metals are M(VI) or d<sup>0</sup>. In addition, the M-C and M-O bonds of the metallacycles in **2**, **4**, **6**, and **8** would be considered as ionic (C<sup>-</sup> or O<sup>-</sup>), so that these metals are also M(VI) or d<sup>0</sup>. Such a formalism has the advantage of being simple and unambiguous; however, we believe that it is oversimplified.

Our wave functions indicate that the M-Cl bonds for **1-8** are indeed quite ionic and suggest that the Cl can rather accurately be pictured as chloride ions, Cl<sup>-</sup>. However, the remaining bonds in **1-8** are quite covalent and should be viewed as involving localized d orbitals on the metal paired into valence bonds with appropriate ligand orbitals. Since each d orbital is paired with a different ligand orbital, the four d electrons are in different orbitals. Thus the electron density distributions on the metals for **5-8** are all best described as high-spin d<sup>4</sup> configurations [M(II)] rather than d<sup>0</sup> configurations [M(VI)]. However, since each of these d orbitals is involved in a bond pair with a ligand orbital, the spectroscopic transitions are expected to correspond essentially one-to-one with those that would have arisen from a d<sup>0</sup> configuration with the bond pairs each completely ionic toward the appropriate ligand.

Because of the usual oxidation state formalism, the CR<sub>2</sub> group of **1** or **7** is often referred to as <sup>2-</sup>CR<sub>2</sub>. We want to emphasize that this description is not a good approximation to the actual form of the wave functions. We find that the M=CR<sub>2</sub> bond is a very covalent double bond involving (i) a dσ orbital in the metal paired with a hybridized carbon orbital (sp<sup>2</sup>σ) and (ii) a dπ orbital on the metal paired with a pπ orbital on the carbon. Thus the bond is an ordinary double bond (analogous to that in olefin) and the CR<sub>2</sub> part of the system is essentially identical with the ground state of a simple alkylidene or carbene (one electron in sp<sup>2</sup>σ and one in pπ combined to yield a triplet state). Consequently, we recommended that the M=CR<sub>2</sub> bond be described as a metal alkylidene double bond.

The bonding in the metal-CR<sub>2</sub> compounds discussed above (all high-valent metals) is quite different from that in the low-valent systems (CO)<sub>5</sub>WCPH<sub>2</sub>. In the latter case, the CPH<sub>2</sub> has the character of a singlet carbene with an empty pπ orbital and a doubly occupied σ orbital (sp<sup>2</sup>σ) pointing at the metal. Thus the bond here is basically a coordinate bond (not unlike that in CO) with possible dπ back-bonding (as also in CO). As a result, there is a very low rotational barrier here. In contrast, the high-valent systems lead to a σ bond and a π bond between metal and CR<sub>2</sub> and exhibit high rotational barriers.

We should note here that the above very covalent description of the M=O, M=CR<sub>2</sub>, M-O, and M-C bonds is contingent upon having at least two ionic bonds to the metal (M-Cl here). The ionic character in these two bonds makes the metal positive and unwilling to lose further electrons to the O or C groups. Similar behavior is expected if the two Cl<sup>-</sup> are replaced by two other electronegative ligands, e.g., F<sup>-</sup>, <sup>-</sup>OR, or even cyclopentadienyl anions. However, if the Cl ligands are replaced by alkyl groups, the M=O and M-O bonds are expected to become much more ionic, reducing or eliminating the triple character found in **3**, **6**, and **8**.

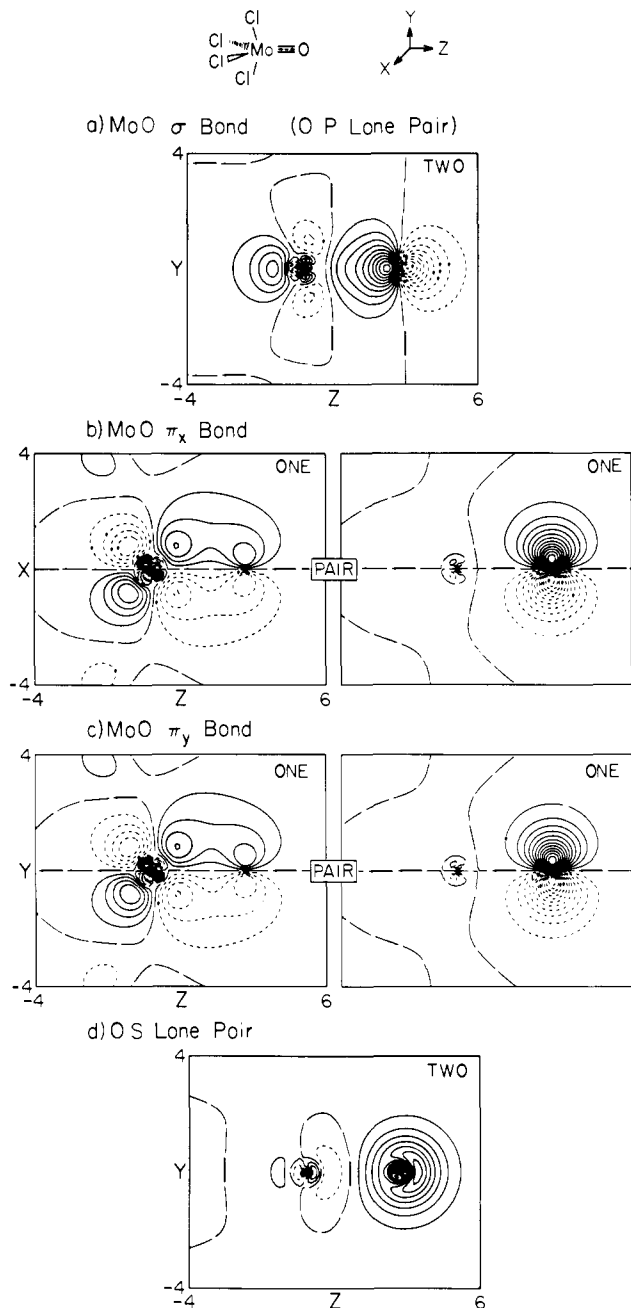


Figure 5. The GVB orbitals involved in the oxo bond of Cl<sub>4</sub>Mo=O.

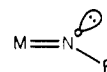
Other ligands may also perform analogously to the spectator oxo group in stabilizing the metallocycle, e.g., **7** to **8**. For example, we find that an imino group NR can form a triple bond to the metal



with two π bonds and a donor-acceptor σ bond analogous to



in **3**, **6**, or **8** or a double bond (π and σ) to the metal



analogous to M=O in **5** and **7**. However, the spectator imino stabilization appears to be approximately half as great as spectator oxo stabilization. This smaller stabilization could be an advantage since it might allow metathesis *without* the need for a Lewis base

Table I. Energies for Bimolecular Decomposition Modes of Oxo-Alkylidenes (6), (7), and (8)

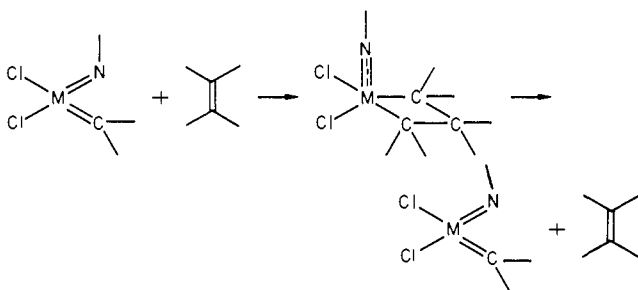
M	olefin formation (6)	ketone formation (7)	dioxygen formation (8)
Cr	-44	-44	+15
Mo	-6	-1	+69
W	-2	+3	+73

Table II. Trends in Bond Strength (kcal/mol) within the Same Row

molecule	bond strength	difference Ti to Cr
(Cl) <sub>2</sub> Ti-O	140 <sup>b</sup>	-89
(Cl) <sub>2</sub> (O)Cr-O	51 <sup>b</sup>	
(Cl) <sub>2</sub> Ti-CH <sub>2</sub>	78 <sup>b</sup>	-30
(Cl) <sub>2</sub> (O)Cr-CH <sub>2</sub>	48 <sup>b</sup>	
Ti-(O- <i>t</i> -Bu) <sub>4</sub>	104 <sup>a</sup>	
V-(O- <i>t</i> -Bu) <sub>4</sub>	90 <sup>a</sup>	-32
Cr-(O- <i>t</i> -Bu) <sub>4</sub>	72 <sup>a</sup>	

<sup>a</sup> Average bond energy, from ref 36. <sup>b</sup> Theoretical calculations.

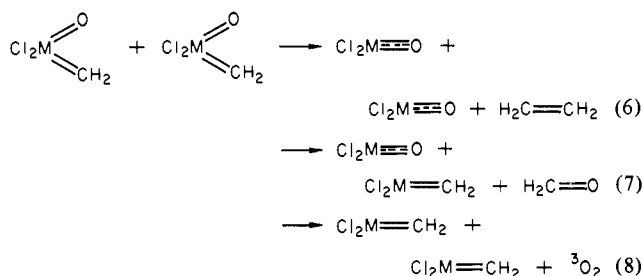
(see sections E and F). Thus both metallacycle formation and decomposition



might be approximately thermoneutral.

Other possible spectator ligands for metallacycle stabilization are alkoxy and sulfo ligands; however, we have not yet tested these cases.

**D. Chain Termination Steps.** In analyzing the possible role of oxo-alkylidene intermediates in reactions, we should consider the possible chain termination steps (6)–(8). As indicated in Table



I, the W species is most stable with respect to reactions 6 and 7, Mo is slightly less favorable, and Cr is quite unfavorable.

A second decomposition mode (which cleanly differentiates the chemistry anticipated for Cr from the chemistry anticipated for Mo and W) is the reductive elimination pathway (c of Scheme I). For Cr this pathway (leading to cyclopropane) is energetically accessible and hence the Cr oxo-alkylidene should *not* form a stable, high-valent metathesis catalyst. In contrast, for the Mo and W oxometallobutanes, metathesis will dominate reductive elimination (cyclopropane formation). As discussed previously,<sup>17</sup> the origin of this dramatic difference is the increased bond strengths in Mo complexes and a further increase for W compounds. This is due to the general trend that transition-metal-ligand bond strengths decrease as one moves across the periodic table from the left to the right and increase as one moves down a column. Examples of this are shown in Tables II and III. These trends arise because metal-ligand orbital overlaps *decrease* as one

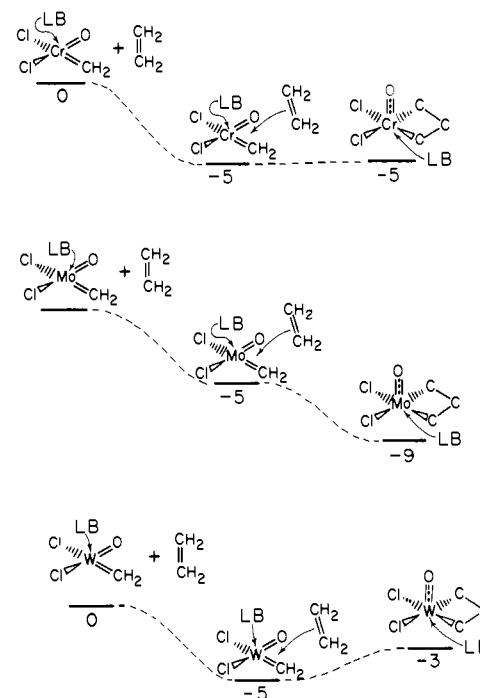
Table III. Trends in Bond Strength (kcal/mol) within the Same Column

molecule	bond strength	difference	
		1st to 2nd	2nd to 3rd
(Cl) <sub>2</sub> (O)Cr-O	51 <sup>b</sup>		
(Cl) <sub>2</sub> (O)Mo-O	79 <sup>b</sup>	28	
(Cl) <sub>2</sub> (O)Cr-CH <sub>2</sub>	48 <sup>b</sup>		
(Cl) <sub>2</sub> (O)Mo-CH <sub>2</sub>	71 <sup>b</sup>	23	
Ti-(O- <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub>	106 <sup>a</sup>		
Zr-(O- <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub>	126 <sup>a</sup>	20	4
Hf-(O- <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub>	130 <sup>a</sup>		

<sup>a</sup> Average bond energy, from ref 36. <sup>b</sup> Theoretical calculations.<sup>21</sup>

Table IV. GVB Orbital Overlaps for Metal-Alkylidene Bonds

molecule	$\sigma$ bond	$\pi$ bond
(Cl) <sub>2</sub> Ti-CH <sub>2</sub>	0.74	0.41
(Cl) <sub>2</sub> (O)Cr-CH <sub>2</sub>	0.60	0.39
(Cl) <sub>2</sub> (O)Mo-CH <sub>2</sub>	0.74	0.53



**Figure 6.** Effect of a Lewis base (LB) and  $\pi$  complexation of the olefin upon the energetics ( $\Delta G_{300}$  in kcal/mol) for the reaction of C<sub>2</sub>H<sub>4</sub> with oxo-alkylidenes.

goes across a row of the periodic table and *increase* as one goes *down* a column. (This in turn results from general trends in sizes of d orbital.) Table IV shows the  $\sigma$  and  $\pi$  bond overlaps for three complexes, verifying this effect.

**E. Solvation Effects.** In order to relate our theoretical studies to the experimentally relevant systems, it is necessary to include possible differential effects due to solvation. Fortunately the postulated intermediates are uncharged and the solvents used for metathesis are aprotic solvents such as benzene, chlorobenzene, hexane, or CCl<sub>4</sub>, for which estimates of solvation effects are most straightforward. Little in the way of quantitative data on such effects is yet available; however, some preliminary calculations provide a basis for estimates.

From studies on the interaction of Cl<sub>2</sub>Ti-O with H<sub>2</sub>C=CH<sub>2</sub>, we find a complexation enthalpy of 18 kcal. This interaction depresses the reactant side effects of the cycloaddition reactions 1–5 by a corresponding amount. Similar calculations are underway for models of the Cr and Mo complexes where this effect is ~10–15 kcal.

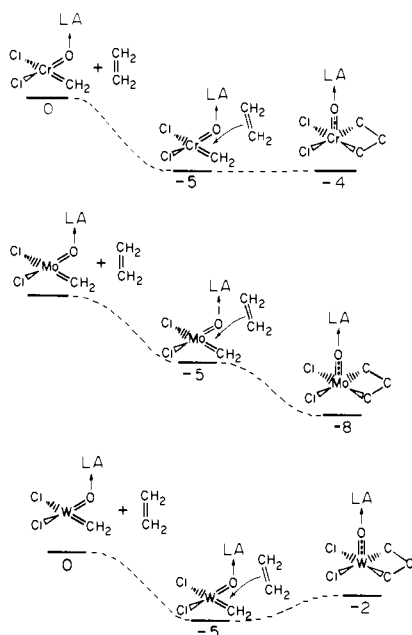


Figure 7. Effect of a Lewis acid (LA) and  $\pi$  complexation of the olefin upon the energetics ( $\Delta G_{300}$  in kcal/mol) for the reaction of  $C_2H_4$  with oxo-alkylidenes.

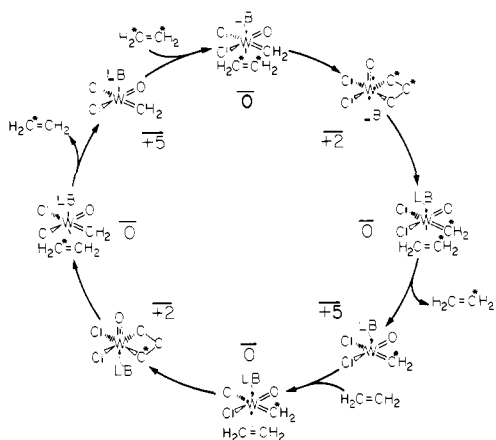


Figure 8. The full catalytic cycle for metathesis by W oxo-alkylidene with Lewis base present (energies are  $\Delta G_{300}$  in kcal/mol).

In addition, metathesis solutions generally contain Lewis bases such as  $Cl^-$ , amines, or phosphines which we find to cause differential effects<sup>25</sup> on reactions 1–5. For example, complexation of a phosphine to species such as 6 and 8 is<sup>26a</sup> about half of that to species 5 and 7. Further, metathesis solutions often contain Lewis acids such as aluminum alkyl chlorides that we find<sup>26b</sup> to cause differential effects ( $\sim 16$  kcal) on species 7 and 8.

**F. The Mechanism.** Combining the estimated solvation effects with the calculated (gas-phase) energetics leads to the energetics

(25) (a) Variation of Lewis base does produce differential effects on the rate of metathesis; see, for example, ref 24. (b) This is verified by a shortening of both the M–O and M–C double bonds by  $\sim 0.05$  Å. The strengthening of the W–C and W–O bonds is apparent from the *shortening* of these bonds in going from  $Cl_2W(O)(CH_2)$  to  $Cl_2W(O)(CH_2)(PR_3)$ . This is followed by a lengthening of the W–C and W–O bonds in going to  $Cl_2W(O)(CH_2)(PR_3)_2$  due to increased steric interactions.

(26) (a) A difficulty in determining the binding energy of olefins or other Lewis bases to  $d^0$  metal complexes is that they are usually irreversibly oxidized. See D. J. Salmon and R. A. Walton, *Inorg. Chem.*, **17**, 2379–2382 (1978). An exception to this is  $TiCl_4$  where several Lewis acid–base complexation energies have been determined (28–45 kcal). See B. Hessel and P. G. Perkins, *J. Chem. Soc. A*, 3229–3234 (1970). (b) We have determined the binding energies for  $Cl_3Al-OC$  and  $Cl_3Al-OCH_2$  to be 14.4 and 30.7 kcal, respectively. As the oxygen atoms in OC and in  $OCH_2$  are quite analogous to those in  $MoCl_5O$  and  $Cl_2MoO_2$ , the differential binding found (16.3 kcal) should provide a reasonable estimate of the differential effect provided by Lewis acids.

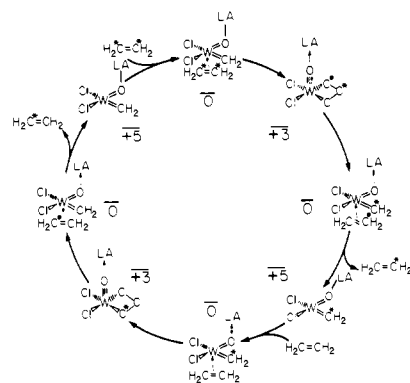


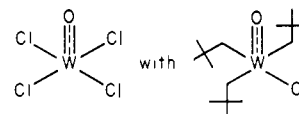
Figure 9. The full catalytic cycle for metathesis by W oxo-alkylidene with Lewis acid present (energies are  $\Delta G_{300}$  in kcal/mol).

in Figure 6 (Lewis bases) and Figure 7 (Lewis acids) for Cr, Mo, and W. The resulting catalytic cycles are illustrated for W in Figures 8 and 9. These studies suggest the importance of balance between the metal (W here), the other ligands around the metal (Cl here), the Lewis acid or base, and the solvent. Changes in these quantities could lead to a large  $\Delta G$  for one or another of the steps and to a large decrease in the rate of reaction.

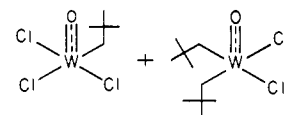
### Discussion of Experimental Results

**A. The Role of Oxygen.** Several experiments provide evidence confirming our findings that the stable, high-valent metathesis catalyst is an oxo-alkylidene. First, Basset et al.<sup>18</sup> found that oxygen-containing compounds ( $O_2$  or alcohols) accelerate the metathesis reaction and that chlorine is essential for metathesis. Second, Muetterties<sup>19</sup> and co-workers have shown that catalytic amounts of oxygen are essential for the generation of active stable metathesis catalysts for high-valent tungsten. As discussed in section A of Theoretical Studies, our studies suggest that two electronegative ligands on the metal are important in allowing the spectator oxo group to form the triple bond stabilizing the metallacycle intermediates. However, the chlorine used in our studies (and in the experiments) could probably be replaced by other electronegative ligands such as alkoxides if the carbon portion of the ligand could be made inert. The experiments, which suggested that halide is essential, utilized alkoxide ligands ( $OCH_3$ ), which definitely are not inert to  $\beta$  abstraction and other forms of catalyst degradation.

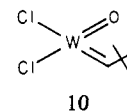
More recently, Osborn<sup>27</sup> and co-workers have generated Mo and W complexes that will metathesize olefins without standard cocatalysts. For example, reaction of



(neither of which will separately catalyze metathesis) leads to a metathesis catalyst. We interpret these results as involving a ligand exchange<sup>28</sup> leading to



followed by  $\alpha$  extraction<sup>29</sup> of either species to yield

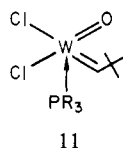


(27) J. R. M. Kress, M. J. Russell, M. G. Wesolek, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 431–432 (1980).

(28) R. A. Walton, *Prog. Inorg. Chem.*, **16**, 1–226 (1972).

which according to our studies should do metathesis.

The most significant experiment establishing the role of oxo-alkylidenes in metathesis was recently reported by Schrock<sup>30</sup> and co-workers. They synthesized high-valent complexes of Mo and W such as

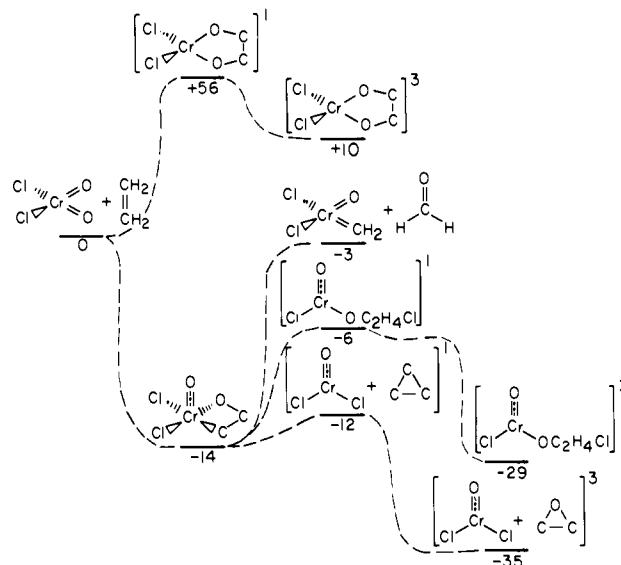


and showed that these complexes metathesize terminal and internal olefins without cocatalysts. Recently, Muettterties has also agreed that metathesis involves an oxo-alkylidene intermediate.<sup>31</sup>

To verify the energetic similarity of dioxo and oxo-alkylidene complexes, we suggest that reaction of ketones with Schrock's oxo-alkylidene complex should generate olefins and a dioxo complex. If isolated, this dioxo complex should react with olefins to regenerate an oxo-alkylidene complex. This reaction has precedent in Tebbe's stabilized titanium-alkylidene complex<sup>32</sup> that has been developed into a reasonable synthetic reagent for the formation of olefins.<sup>33</sup> The titanium system is not reversible due to secondary reactions and the tremendous difference in bond strengths between the oxo and alkylidene complexes for Ti complexes (see Table II).

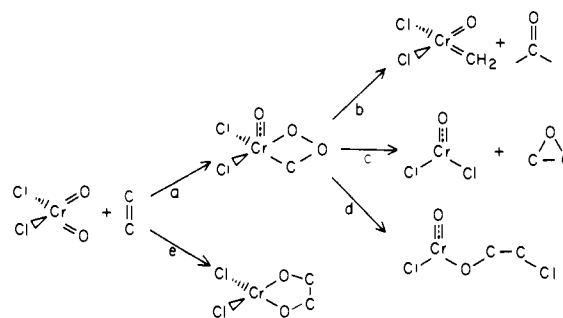
**B. Supported Catalysts.** Based on the theoretical studies, we suggest that molybdenyl and tungstenyl chlorides should be very useful in generating supported catalysts that can be systematically studied [a major difficulty with standard catalyst preparations is that the percentage of metal sites that actually participate in metathesis may be small (~1%)<sup>16</sup>]. Indeed, San Filippo has found that chromyl chloride can be chemisorbed to a support under exceedingly mild conditions and that the chemisorbed chromyl chloride will oxidatively cleave C-C double bonds stoichiometrically.<sup>34</sup> We suggest that low loading of the support will prevent the intermolecular decomposition pathways [d of Scheme I and (4)], allowing metathesis and polymerization pathways to dominate. With the surface loading high, stoichiometric C-C bond cleavage should dominate.

**C. Role of Lewis Acids and Bases.** Some comments on the role of Lewis acids and bases is relevant here. As discussed in section D of Theoretical Studies, we find that the dominant role of the Lewis acid or base is to decrease the gap between the metallacyclic intermediate and the alkylidene complex, thereby decreasing the activation energy for the metalocycle decomposition. Further, the Lewis base increases the electron density at the metal center,<sup>35</sup> strengthening the M-C double bond<sup>25b</sup> and thereby decreasing the importance of the bimolecular decomposition pathways (6)-(8). On the other hand, binding of a *second* Lewis base to the catalyst would inhibit catalysis since the second phosphine must be displaced by the olefin (an endothermic process) before metathesis can begin. Thus our studies suggest that *small amounts* of Lewis base or Lewis acid are *essential* for these high-valent Mo and W complexes to catalyze metathesis; however, *large amounts* of Lewis base can *inhibit* catalysis. These expectations



**Figure 10.** Energetics ( $\Delta G_{300}$  in kcal/mol) for the reaction of  $C_2H_4$  with chromyl chloride.

#### Scheme II



are consistent with current experience.

For example, we suggest that the concentration-dependent rate acceleration<sup>36</sup> inhibition<sup>16</sup> found for amines is due to an initial formation of a monoamine complex that is a better catalyst (as discussed above for phosphines), followed by the eventual formation of the diamine that should be catalytically inactive (this has been shown to be true for phosphines by Schrock).<sup>30,35</sup>

The general accelerating effect of Lewis bases (amines) is well documented for heterogeneous catalysts,<sup>36</sup> again consistent with our expectations. As experimental test of this dual role of phosphines would be to study the rate of catalysis by the Schrock compound **11** as a function of phosphine concentration for very low concentrations. A complication here is the possible use of  $Cl^-$  as a Lewis base in the absence of phosphine.

#### Implications

Our findings have implications for several related homogeneous reactions such as olefin oxidation by  $Cl_2CrO_2$ ,  $KMnO_4$ , and  $OsO_4$  and for the initiation process of the supported metathesis reaction. The homogeneous oxidation reactions will be discussed in subsection A and supported metathesis will be discussed in subsection B.

**A. Olefin Oxidation.** As discussed in section A of Theoretical Studies we find that high valent dioxo complexes (such as  $Cl_2M(=O)_2$ ) will react to form metallacyclooctane intermediate (a of Scheme II). This metallacyclic intermediate can decompose in several ways, it can decompose to form the previously mentioned oxo-alkylidene complex (b of Scheme II), an epoxide (c of Scheme II), or the precursor to a chlorohydrin (d of Scheme II). Each of these products has been observed in alkene oxidation by chromyl chloride.<sup>28,34,37,38</sup>

(29) R. R. Schrock, *Acc. Chem. Res.*, **12**, 98-104 (1979).

(30) (a) R. Schrock, S. Rocklage, J. Wengrovius, G. Rupprecht, and J. Fellmann, *J. Mol. Catal.*, **8**, 73-83 (1980); (b) J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, and W. J. Youngs, *J. Am. Chem. Soc.*, **102**, 4515-4516 (1980).

(31) E. L. Muettterties and E. Band, *J. Am. Chem. Soc.*, **102**, 6574-6575 (1980).

(32) F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *J. Am. Chem. Soc.*, **100**, 3611-3613 (1978).

(33) S. H. Pine, R. Zahler, D. A. Evans, and R. H. Grubbs, *J. Am. Chem. Soc.*, **102**, 3271-3272 (1980).

(34) J. San Filippo, Jr., and C. Chern, *J. Org. Chem.*, **42**, 2182-2183 (1977).

(35) R. R. Schrock and J. Wengrovius, "Symposium on the Chemistry of Early Transition Metal Oxides, Polyoxoanions, and Oxo Complexes", Division of Inorganic Chemistry, Second Chemical Congress of the North American Continent and 180th National Meeting of the American Chemical Society, Las Vegas, NE, Aug 1980.

(36) J. Fathikalajahi and G. B. Willis, *J. Mol. Catal.*, **8**, 127-134 (1980).

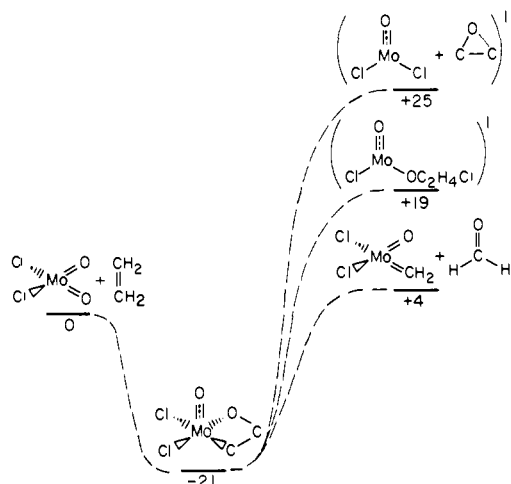
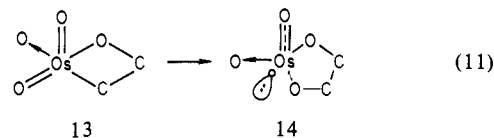
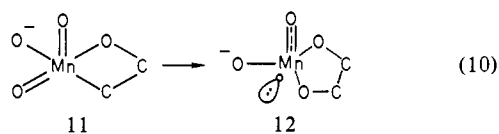
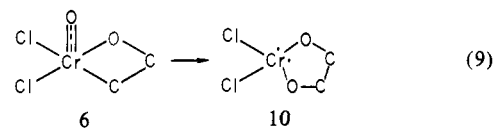


Figure 11. Energetics ( $\Delta G_{300}$  in kcal/mol) for the reaction of  $C_2H_4$  with molybdenyl chloride.

The energetics for the oxidation of ethylene by chromyl chloride are shown in Figure 10. These energetics confirm the proposal (Sharpless<sup>38</sup>) that the metallacyclohexane is a likely common precursor for all of the observed oxygen-containing products and rule out the direct addition (ene) reaction characteristic of oxidation by  $KMnO_4$ ,<sup>39</sup> and  $OsO_4$ ,<sup>40</sup> (e of Scheme II). It is noteworthy that  $Cl_2CrO_2$  does not react to form significant diol product, whereas  $KMnO_4$  and  $OsO_4$  dominantly form diols without significant epoxide formation. This differential reactivity is easily understood in terms of stabilization due to spectator oxo groups. Starting from the respective metallacyclohexane intermediates<sup>41</sup>



the difference is apparent. That is, for  $Cl_2CrO_2$  the shift involves reaction with a strong metal oxo triple bond, preventing (9), whereas for both  $KMnO_4$  and  $OsO_4$  the reaction is with an oxo double bond with a spectator oxo converting to an oxo triple bond

(37) F. Freeman, C. R. Armstead, M. G. Essig, E. L. Karchefski, C. J. Kojima, V. C. Manopoli, and A. H. Wickman, *J. Chem. Soc., Chem. Commun.*, 65 (1980).

(38) K. B. Sharpless, A. Y. Teranishi, and J. E. Backvall, *J. Am. Chem. Soc.*, **99**, 3120–3128 (1977).

(39) (a) R. Stewart, "Oxidation in Organic Chemistry", Part A, K. B. Wiberg, Ed., Academic Press, New York, 1965, pp 1–68; (b) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Menlo Park, CA, 1972, pp 257–291; (c) D. M. Walba, M. D. Wand, and M. C. Wilkes, *J. Am. Chem. Soc.*, **101**, 4398–4399 (1979); (d) J. E. Baldwin, M. L. Crossley, and E. M. Lehtonen, *J. Chem. Soc., Chem. Commun.*, 918–920 (1979); (e) E. Klein and W. Rohahn, *Tetrahedron*, **21**, 2353–2358 (1965).

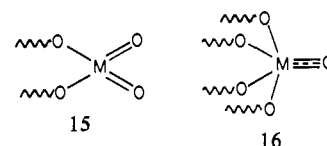
(40) (a) M. Schröder, *Chem. Rev.*, **80**, 107–213 (1980); (b) K. B. Sharpless, C. A. Chong, and K. J. Oshima, *J. Org. Chem.*, **41**, 177–179 (1976); (c) E. Herranz and K. B. Sharpless, *ibid.*, **43**, 2544–2548 (1978); (d) E. Herranz, S. A. Biller, and K. B. Sharpless, *J. Am. Chem. Soc.*, **100**, 3596–3598 (1978); (e) E. Herranz and K. B. Sharpless, *J. Org. Chem.*, **45**, 2710–2713 (1980).

(41) Here the arrow in (11) indicates a d lone pair on the metal making a donor-acceptor bond to a closed-shell oxygen atom (doubly occupied  $\pi$  orbitals, empty  $p\sigma$  orbital).

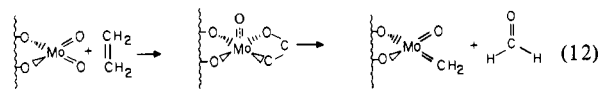
thus enhancing (10) and (11) and driving the formation of species **12** and **14**. (These latter two systems may go directly to **12** or **14** without passing through **11** or **13**.)

As discussed in section C of Theoretical Studies, a major difference between Cr and Mo compounds is the general increase in bond strength of 15 kcal per bond. This effect manifests itself in strong relative disfavoring of any reductive elimination pathway for molybdenum. For Mo, the C–C bond cleavage pathway will dominate the reductive elimination of epoxides or chlorohydrins, and (as will be discussed in section B) it is likely through this pathway that  $MoO_3$  and  $WO_3$  are activated for metathesis on a polymer support. The energetics for these processes are summarized in Figure 11 for molybdenum.

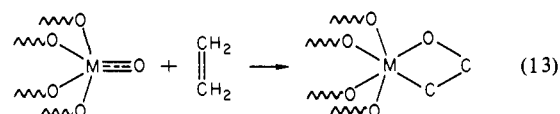
**B. Supported Catalysts.** An understanding of the precise character of the surface sites responsible for heterogeneous metathesis is of both general mechanistic and industrial interest. A precise understanding of sites and mechanism could be useful in developing modified procedures allowing more economical activation of the surface with a possible increase in the concentration of active catalytic sites (currently  $\sim 1\%$ ). The two most likely surface sites on calcined molybdates or tungstenates are **15** and **16**, where **15** is analogous to **5** and **16** is analogous to **3**. Ener-



getically these two surface sites are quite similar.<sup>42</sup> Although these sites lead to very similar physical characteristics (e.g., the metal–oxygen stretching frequency is very similar),<sup>43</sup> they should lead to enormous differences catalytically. Thus species **15** should react with olefins to form oxo-alkylidenes (see eq 12), whereas



species **16** should be inert to attack at the oxo group since the metallacyclohexane intermediate (eq 13)



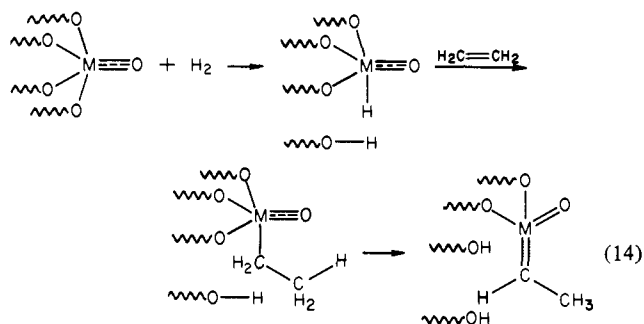
should be energetically inaccessible ( $\Delta G \approx +44$  kcal). Thus we are suggesting that if the surface is prepared in a manner that maximizes the concentration of species **15** an active metathesis catalyst will be generated simply by the addition of olefin, even at room temperature! In fact, we believe that this *has* been experimentally observed. Recently, Hall<sup>44</sup> has found that there is a concentration dependence to the reaction pathway for olefins over supported  $WO_3$ . At low olefin concentrations, olefin isomerization is observed, while at high olefin concentration, metathesis occurs.<sup>44</sup> Our interpretation of these results is as follows. If the surface sites are mainly species **16**, activation to species **15** is required. Two possible procedures involve  $H_2$  and a final abstraction process. The first possibility (eq 14) involves addition of  $H_2$  across an M–O bridge bond, followed by olefin addition across the M–H bond, leading to an alkyl group (ethyl in this case) that can undergo an  $\alpha$  abstraction to yield an oxo-carbene that

(42) We estimate that **15** is  $\sim 2$  kcal less stable than **16**. However, the uncertainties in this estimate (due to use of Cl to represent bridged oxygen and ignoring adjacent surface sites) are probably  $\sim 10$  kcal.

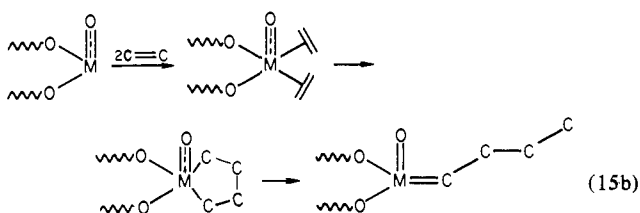
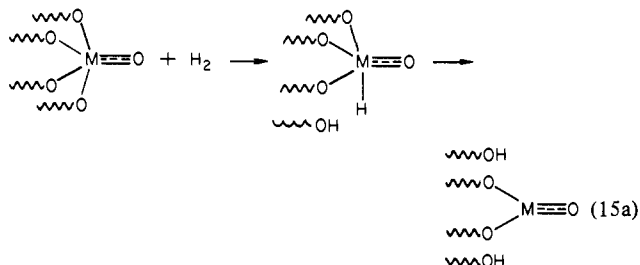
(43) H. Jezlorowski and H. Knözinger, *J. Phys. Chem.*, **83**, 1166–1173 (1979).

(44) J. Goldwasser, J. Engelhardt, and W. K. Hall, *J. Catal.*, **70**, 275–286 (1981); J. Engelhardt, J. Goldwasser, and W. K. Hall, *ibid.*, **70**, 364–374 (1981); J. Goldwasser, J. Engelhardt, and W. K. Hall, *ibid.*, **71**, 381–388 (1981).





can catalyze metathesis. The second possibility (eq 15) involves an overall reduction of the metal [formally to M(IV)], (15a),



followed by reaction with two olefins to form a metallacyclopentane that could undergo internal  $\alpha$  abstraction to give the oxo-alkylidene complex, (15b). The rates of these three possible

initiation processes, (13), (14), and (15), should depend upon reaction conditions; each may occur in some systems. Since these processes yield different products, it should be possible to design experiments to test these predictions and to establish which occur in various circumstances.

### Summary

In summary, we suggest that oxo-alkylidene complexes are the stable metathesis catalysts for high-valent Mo, W, and Re complexes and that the oxygen ligand is intimately involved in the catalytic process. Furthermore, we suggest that similar oxo-alkylidene complexes can be formed on supported catalysts and that dioxo precursors may provide a convenient route to formation of well-defined surface catalysts for olefin metathesis and oxidation reactions. The spectator oxo group is suggested to play a central role in stabilizing the critical intermediate in these reactions and may be important in other reactions of metal oxides ( $\text{MnO}_4^-$ ,  $\text{OsO}_4$ ,  $\text{RuO}_4$ , supported transition-metal oxides).

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**Registry No.** 3 (M = Cr), 57414-29-6; 3 (M = Mo), 13814-75-0; 5 (M = Cr), 14977-61-8; 5 (M = Mo), 13637-68-8; 6 (M = Cr), 79899-75-5; 6 (M = Mo), 79899-76-6; 6 (M = W), 79899-77-7; 7 (M = Cr), 74670-62-5; 7 (M = Mo), 74670-63-6; 7 (M = W), 75213-82-0; 8 (M = Cr), 79899-78-8; 8 (M = Mo), 79899-79-9; 8 (M = W), 79899-80-2;  $(\text{Cl}_2)\text{Ti}-\text{O}$ , 13780-39-7;  $(\text{Cl}_2)\text{Ti}-\text{CH}_2$ , 79899-81-3;  $\text{Ti}-(\text{O}-i\text{-Bu})_4$ , 3087-39-6;  $\text{V}-(\text{O}-i\text{-Bu})_4$ , 10585-27-0;  $\text{Cr}-(\text{O}-i\text{-Bu})_4$ , 10585-25-8;  $\text{Ti}-(\text{O}-i\text{-C}_3\text{H}_7)_4$ , 546-68-9;  $\text{Zr}-(\text{O}-i\text{-C}_3\text{H}_7)_4$ , 2171-98-4;  $\text{Hf}-(\text{O}-i\text{-C}_3\text{H}_7)_4$ , 2171-99-5;  $\text{C}_2\text{H}_4$ , 74-85-1.

## Functionally Polymerized Surfactant Vesicles. Synthesis and Characterization

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**Abstract:** Bis[2-(10-undecenoyloxycarbonyl)ethyl]dimethylammonium bromide (1), bis[2-(10-undecenoyloxycarbonyl)ethyl](2-hydroxyethyl)methylammonium bromide (2), bis[2-(10-undecenoyloxycarbonyl)ethyl]amidophosphoric acid (3), bis[2-(10-undecenoyloxycarbonyl)ethyl]-2-sulfoethylamine (4), allylbis[2-(dodecanoyloxycarbonyl)ethyl]methylammonium bromide (5), and dimethyl-*n*-hexadecyl[10-(*p*-vinylcarboxanilido)decyl]ammonium bromide (6) have been synthesized. The predominantly single compartment bilayer vesicles formed from these surfactants could be polymerized either by exposure to ultraviolet irradiation or by the use of azoisobutyronitrile (AIBN) as an initiator. The presence of vesicles (unpolymerized and polymeric) has been demonstrated by electron micrography,  $^1\text{H}$  NMR, gel filtration, phase transition, turbidity changes, substrate entrapment, and permeability. Rates of light initiated polymerization of vesicles prepared from 6 have been found to be first order ( $k = 0.10 \text{ min}^{-1}$  at 25 °C;  $[\mathbf{6}] = 0.33$  and 0.20 mg/1.0 mL of  $\text{H}_2\text{O}$ ) and independent of the concentration of 6. Under identical conditions, polymerization of 6 in methanol has occurred at a very much slower rate, and no polymerization has been observed at higher concentrations (2 mg of 6/2 mL of MeOH). Polymerized vesicles are considerably more stable and less permeable and have reduced rates of turbidity changes compared to their unpolymerized counterparts.

Completely synthetic surfactant vesicles<sup>1</sup> are increasingly being utilized in photochemical solar energy conversion,<sup>2</sup> reactivity

control,<sup>3</sup> and drug delivery.<sup>4</sup> Recognizing the need for enhanced stability, Regen reported the first synthesis of a polymerized surfactant vesicle from  $(\text{CH}_3)_2\text{N}^+(\text{C}_{16}\text{H}_{33})[(\text{CH}_2)_{11}\text{OC}(=\text{O})\text{C}-$

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